

Dynamic Mechanical Thermal Analysis (DMTA) of Polypropylene (PP) Containing Decabromodiphenyl Ether (DBDE) and Glycerol

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Abstract: Three series of Polypropylene (PP) specimens, namely series A (without glycerol), B (with 5% glycerol) and C (with 10% glycerol) with various percentage of Decabromodiphenyl Ether (DBDE), were studied using Dynamic Mechanical Thermal Analyzer (DMTA). For series A specimen, pure PP (0% glycerol and 0% DBDE) yield the highest storage modulus E' , and the 2% of DBDE gave the lowest (most degradable) E' . 5% DBDE in series B specimen (5% glycerol) produced the lowest E' while in series C specimen (10% glycerol) 5% DBDE yield the highest E' . For series C specimen, 0.5% DBDE yield the lowest E' (the most degradable blend). Below the transition temperature E' did not necessarily decreased systematically with increasing percentage of DBDE for C series specimen.

Key words: Storage modulus (E'), decabromodiphenyl ether (DBDE) and glycerol

Introduction

Plastic, a type of polymer, has a variety of usage such as packaging and household articles. Its resistance to environmental attack is an advantage for most applications. Nevertheless, disposal of solid plastics waste from homes, offices and factories contribute considerably to the solid waste disposal problems. This is a major problem in large cities mainly due to plastic high degree of nondegradability.

Recycling and reusing synthetic polymer such as plastic become the most acceptable way to solve waste problem. Recycling is economical but it is not generally cost effective to recycle common polymers such as Polypropylene (PP) and Polystyrene (PS). This is due to the low intrinsic values of the recovered materials. Therefore, degradable polymer has become an alternative way to solve the waste disposal problems. PP ranked third in the production of plastics after Polyethylene (PE) and Poly Vinyl Chloride (PVC). Due to its cost effectiveness, versatility, overall competitiveness and excellent environment aspects, PP is the fastest growing plastics (Feldman and Barbalata, 1996). PP is a crystalline polymer with melting temperature (T_m) at 176°C and the glass transition temperature (T_g) at 10°C.

Addition of additives may alter the properties of polymer, such as producing harder or flexible polymer either prevent or promote degradations. Polymer degradations are not new. There are several everyday examples of polymer degradations such as the deterioration of cellulose in wood, rubber in car tires and the cracking and yellowing of paint films. Degradation

processes vary and it is depended on the structure of the polymer, manufacturing history and environmental conditions in which the polymer is used.

Degradation is defined as breakdown of complex structure into simpler compounds by the influence of chemical and/or physical factors (Rabek, 1987). Physical changes due to degradation include decrease in molecular weight, tensile strength, impact strength, elongation at break, lose of gloss and surface erosion. Stability to sunlight exposure is one of the most important criteria in determining the practical applications of all polymeric materials for outdoor purposes. All un-stabilized organic polymers oxidize and/or degrade upon exposure to sunlight in the presence and/or absence of oxygen.

Yichao Lin (1997) showed the effects of cerium carboxylate (CeCar_3) with or without aromatic ketones on the carbonyl indices of photo oxidation of Low Density Poly Ethylene (LDPE) film. Their results showed that CeCar_3 accelerated photo oxidative degradations of LDPE films and CeCar_3 with aromatic ketones yielded degradation of the films with varying degrees. Tidjani (1997) investigated the environmental and accelerated photo degradation of HDPE and LDPE films. Under natural exposure, the consequences of the oxidation on mechanical properties differed drastically from HDPE to LDPE.

Torikai *et al.* (1993) investigated the photo degradation of PP (containing 2% by weight of decabromodiphenyl ether, DBDE) by monochromatic light of wavelengths 260, 280, 300, 320, 340 and 360 nm. Their results indicated that the addition of DBDE accelerated the photo degradation of PP.

The objective of this work was to study the effect of DBDE (as a flame-cut agent) and glycerol (as the plasticizer) on the dynamic mechanical properties of PP and to obtain the optimum percentage of DBDE and glycerol that yield the lowest E' which enhance physical degradation.

Materials and Methods

PP (806063), a product from Polypropylene Malaysia Sendirian Berhad, was used with DBDE and glycerol. DBDE ($\text{C}_{12}\text{Br}_{10}\text{O}$) was purchased from Fluka Chemie, AGCH-9470 Buchs in the form of powder. It was used, as additive with the T_m over 300°C and no purification was needed before usage. Glycerol ($\text{HOCH}_2\text{CHOHCH}_2\text{OH}$) (2136-03) manufactured by J.T. Baker (U.S.A.) was in the form of liquid and were added during the blending process. Various formulations of the samples prepared are summarized in Table 1.

A Two-Roll Mill machine by Lab Tech. Engineering Co. Ltd. was used to prepare the blends at the temperature of 180°C . A total of 26 grams of mixture (PP, DBDE and glycerol) was blended until melting and homogeneous blends were produced. A Hot and Cold Press machine also made by Lab Tech. Engineering Co. Ltd., was used to press the blends into flat sheets. The temperature applied to the mold was 190°C in four stages. The first stage was a preheating stage where the mold was closed for 4 minutes and the blends begin to melt. The second stage was venting the blend, in order to prevent any gases caught inside the melted polymer blend. This process was hold for 3 seconds. After that, the full pressing stage was maintained for 4 minutes. Finally, the mold was cooled for 4 minutes to complete the process.

Table 1: Various formulations used in the samples preparation

Series	Components	% of DBDE	% of glycerol
A	PP, DBDE	0.0,0.5,1.0,2.0, 5.0	0.0
B	PP, DBDE, Glycerol	0.0,0.5,1.0,2.0,5.0	5.0
C	PP, DBDE, Glycerol	0.0,0.5,1.0,2.0,5.0	10.0

Dynamic Mechanical Thermal Analysis (DMTA) was carried out using Polymer Laboratories Dynamic Mechanical Thermal Analyzer (PL-DMTA Mk 11). Dynamic testing was performed on a 3 5 mm × 10 min × 1 mm rectangular bar in the bending mode. The frequencies applied were 1, 10 and 100 Hz with × 4 strain. Data were taken from - 100 to 100°C with heating rate of 4°C per minute.

Mechanical testing was carried out on Automated Materials Testing System (Instron Universal Testing Machine Series IX). The tensile testing was performed on dumb-bell shaped specimen with a gauge dimension of 50 mm × 3 mm × 1mm in accordance with an ASTM Standard D882.

Results and Discussion

From the quasi-static loading test it is found that the addition 5 and 10% glycerol alone as a plasticizer had softened the pure PP (without DBDE and glycerol) from 1209% elongation at break to 1305 and 1324% respectively (Table 2). Unfortunately this effect was not seen in the dynamic mechanical analysis as shown in Fig. 1.

Table 2: Mechanical properties of the specimen

Series	% DBDE	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
A	0	146.07	35.98	1209.00
	0.5	159.00	37.31	1325.67
	1	163.77	36.61	1314.33
	2	169.87	34.33	1130.67
	5	166.37	31.83	1083.03
B	0	165.03	37.24	1305.00
	0.5	163.40	34.40	1336.54
	1	156.67	35.58	1296.00
	2	162.27	35.23	1243.00
	5	159.73	27.77	1117.33
C	0	165.07	35.85	1324.00
	0.5	161.13	34.93	1412.64
	1	170.43	36.80	1305.00
	2	164.87	33.64	1281.33
	5	162.50	27.31	1098.83

Table 3: Thermal properties for A series specimen

%DBDE	T _g (°C)	T _m (°C)	ΔH (J/g)
0.0	10	165.78	100.35
0.5	16	164.43	98.65
1.0	15	162.11	97.07
2.0	14	159.43	96.83
5.0	15	157.42	92.31

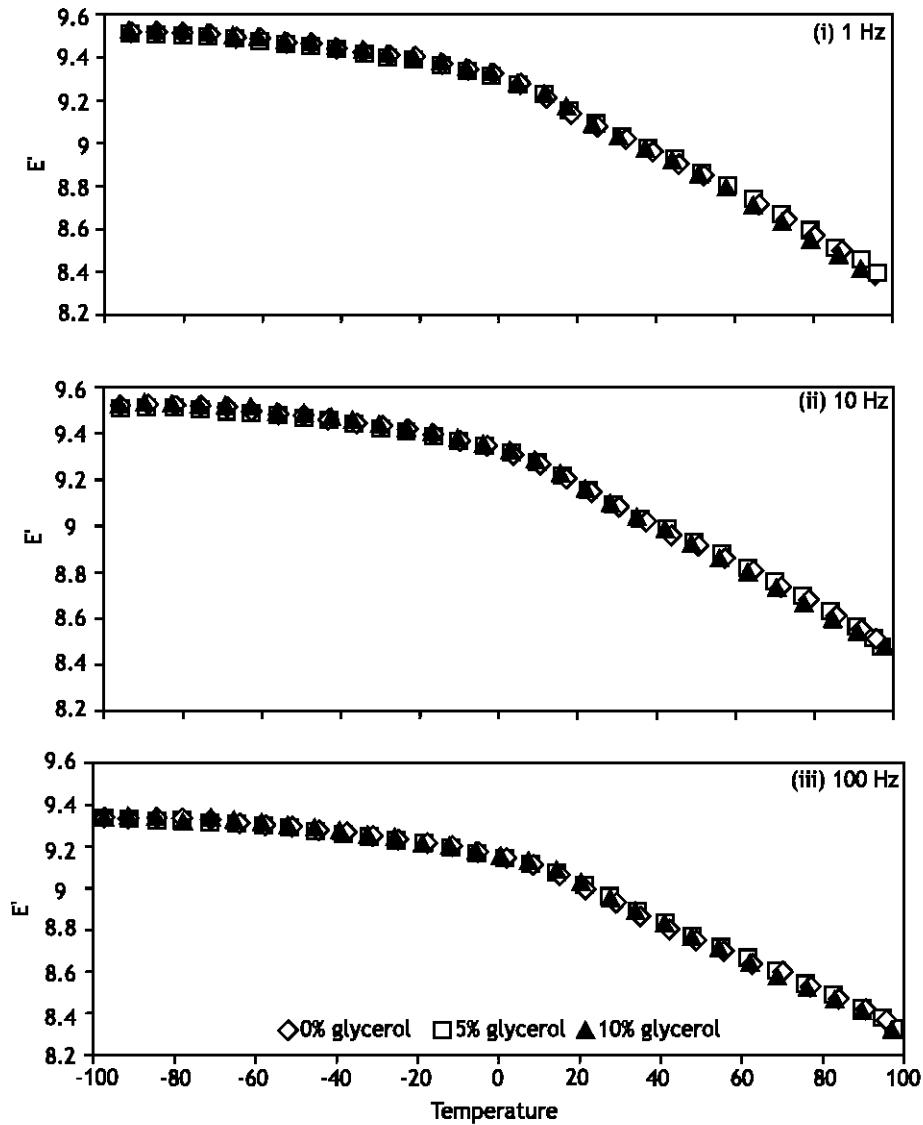


Fig. 1a: E' vs temperature for pure PP (0% DBDE) with various % of glycerol at (i) 1 Hz (ii) 10 Hz (iii) 100 Hz

Glycerol alone (without DBDE) had no effect on the storage modulus (E'). This is shown clearly in Fig. 1a and 1b (the E' and $\tan \delta$ versus temperature respectively for PP specimen without DBDE with various percentage of glycerol at 1, 10 and 100 Hz). Since glycerol alone has no effect on E' values, PP (without glycerol) with various % of DBDE (A series specimens) were scanned using Perkin-Elmer Differential Scanning Calorimeter (PE-DSC). The T_g , T_m and melting enthalpy (ΔH) are shown in Table 3.

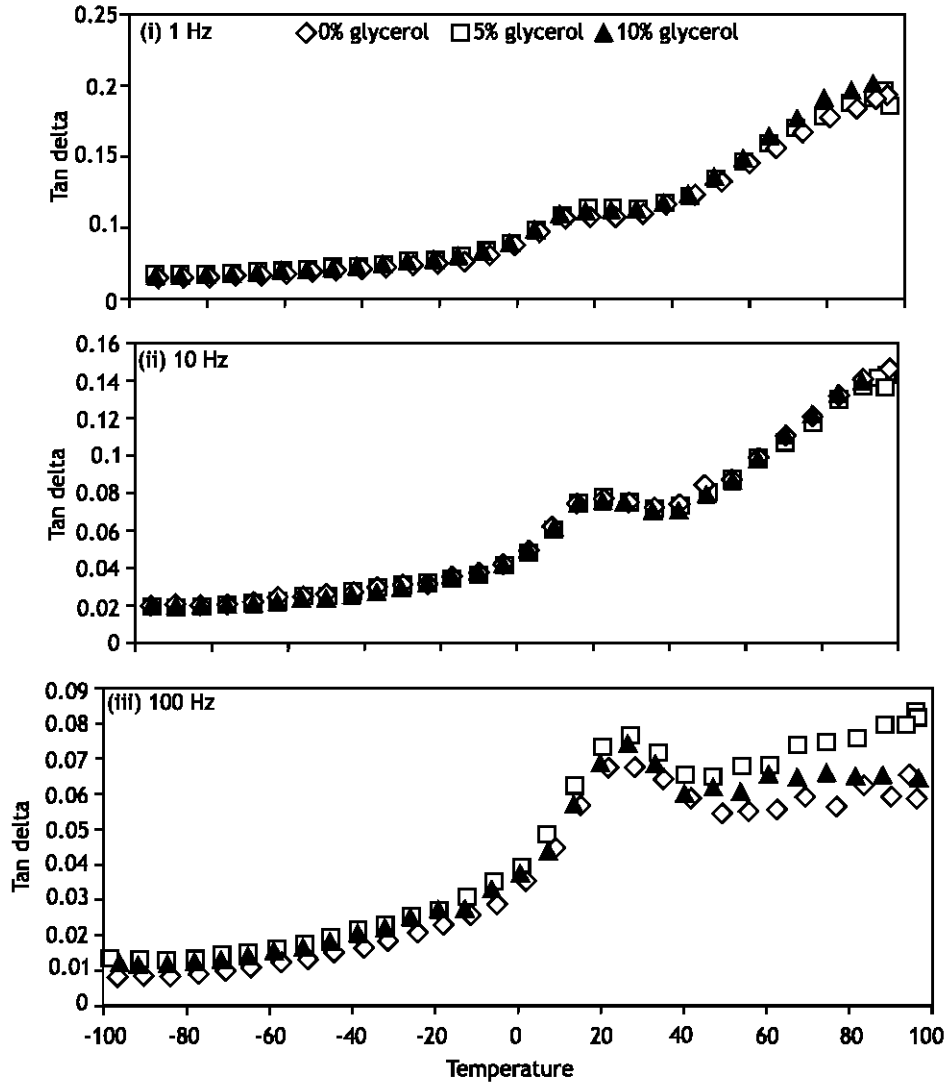


Fig. 1b: Tan delta vs temperature of pure PP (0% DBDE) with various of glycerol at (I) 1 Hz (ii) 10 Hz (iii) 100 Hz

The trend of the changes in T_m and ΔH was thought to be due to the melting of the crystalline part. The constant decrease of ΔH was not consistent with the decreased of E' in the DMTA results.

Fig. 2a and 2b showed the E' and $\tan \delta$ versus temperature respectively for series A specimen (PP without glycerol additive) with various percentage of DBDE at 1, 10 and 100 Hz. Below T_g , pure PP (0% glycerol and 0% DBDE) yielded the highest E' . The addition of 0.5% DBDE decreased E' but as DBDE increased to 1%, E' increase slightly higher than the 0.5% DBDE (although still lower than the pure PP). Further increase of DBDE to 2% yield the minimum E' but surprisingly at 5% DBDE, E' increased again.

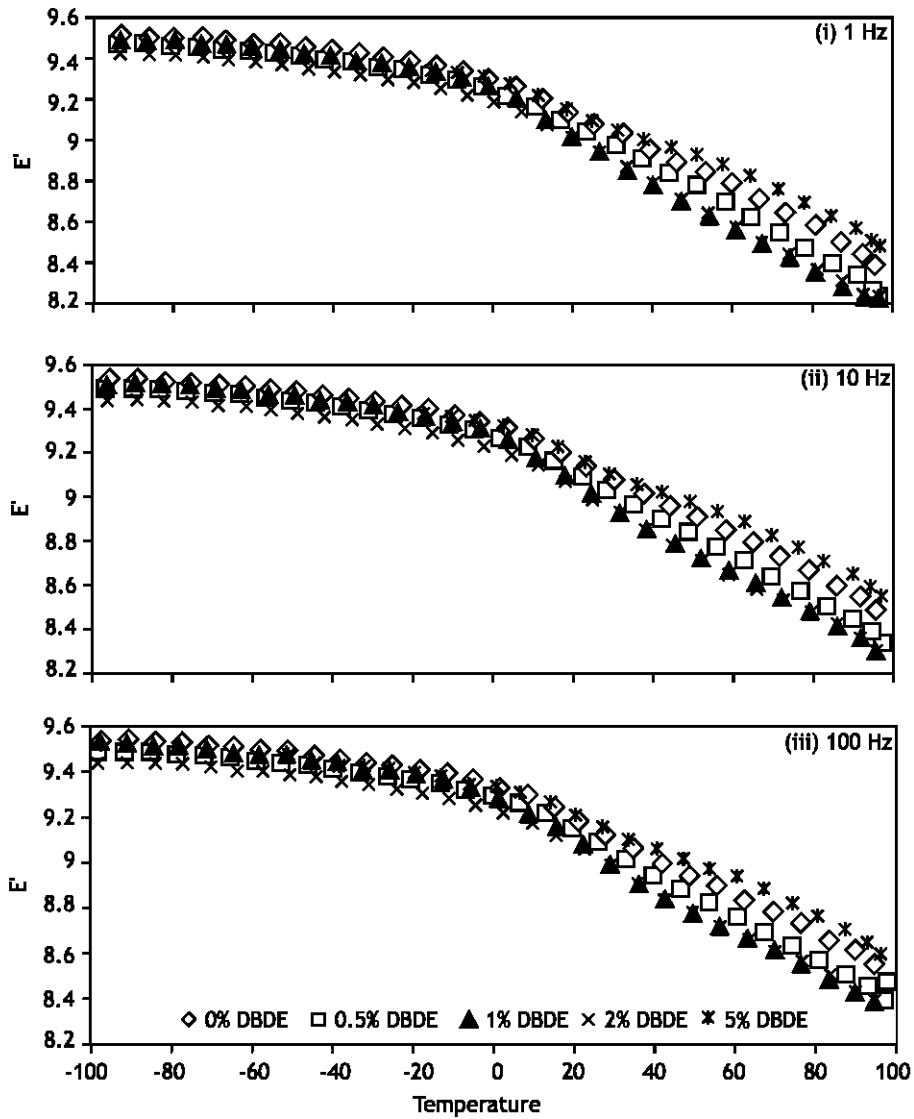


Fig. 2a: E' vs temperature of pure PP (0% glycerol) with various % of DBDE at (i) 1 Hz (ii) 10 Hz (iii) 100 Hz

Above T_g cross over of E' obtained from 1% DBDE blend indicate that the amount of DBDE for degradation is competitive with the 2% DBDE blend. Unfortunately, increasing DBDE to 5% yielded reverse effects, such as strengthened the blend well above the pure PP value. Without the present of glycerol, the effect of DBDE alone showed that 2% DBDE was the optimum amount to be added to pure PP in order to produce the lowest E' values both below and above T_g .

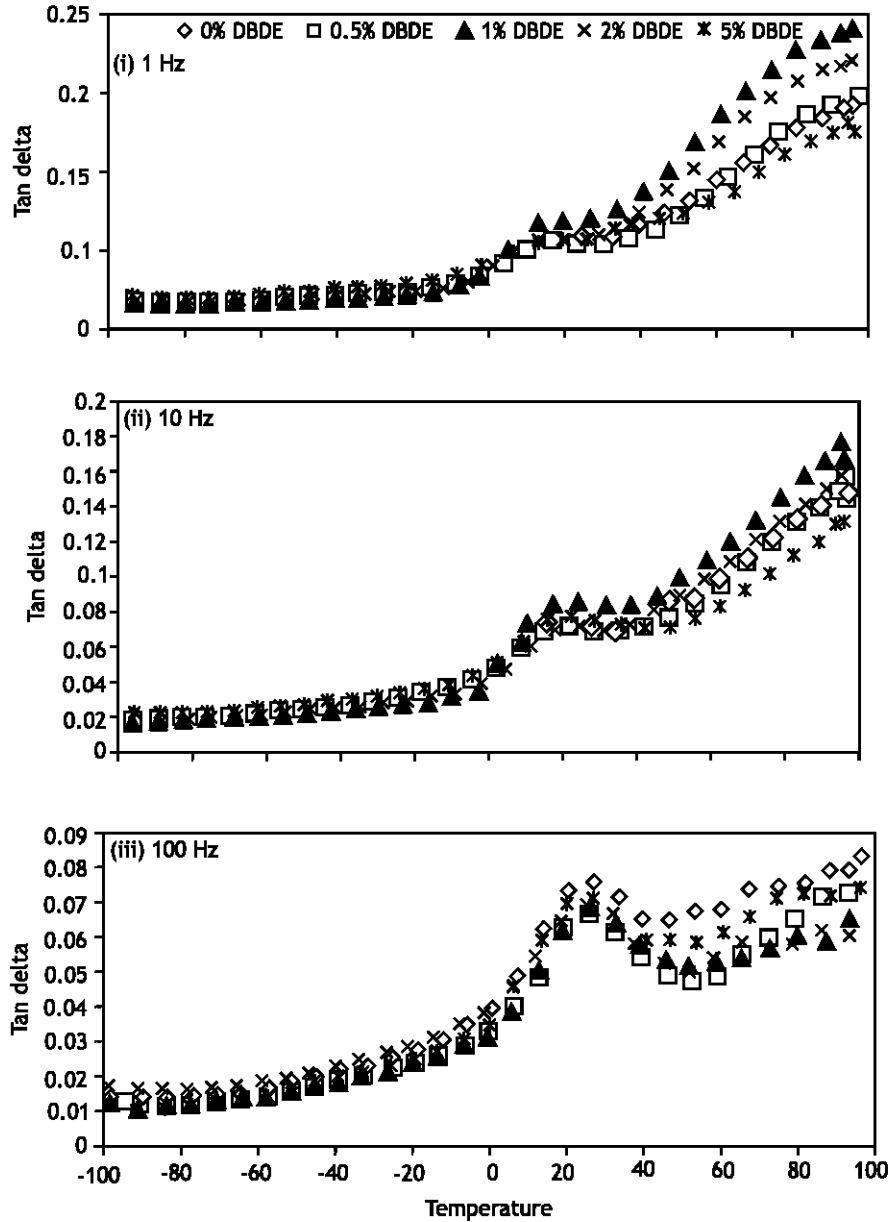


Fig. 2b: Tan delta vs temperature for pure PP (0% glycerol) with various % of DBDE at (I) 1 Hz (ii) 10 Hz (iii) 100 Hz

With the addition of 5% glycerol (Fig. 3a) maximum amount of DBDE (i.e. 5%) degraded the blends to the minimum E' values. As glycerol increased to 10% (Fig. 4a), lower amount of DBDE, as low as 0.5% was efficient enough to decrease the E' values. It was observed that at 10% glycerol, 5% DBDE seem to increase E' higher than pure PP although a cross over occur above T_g . Below

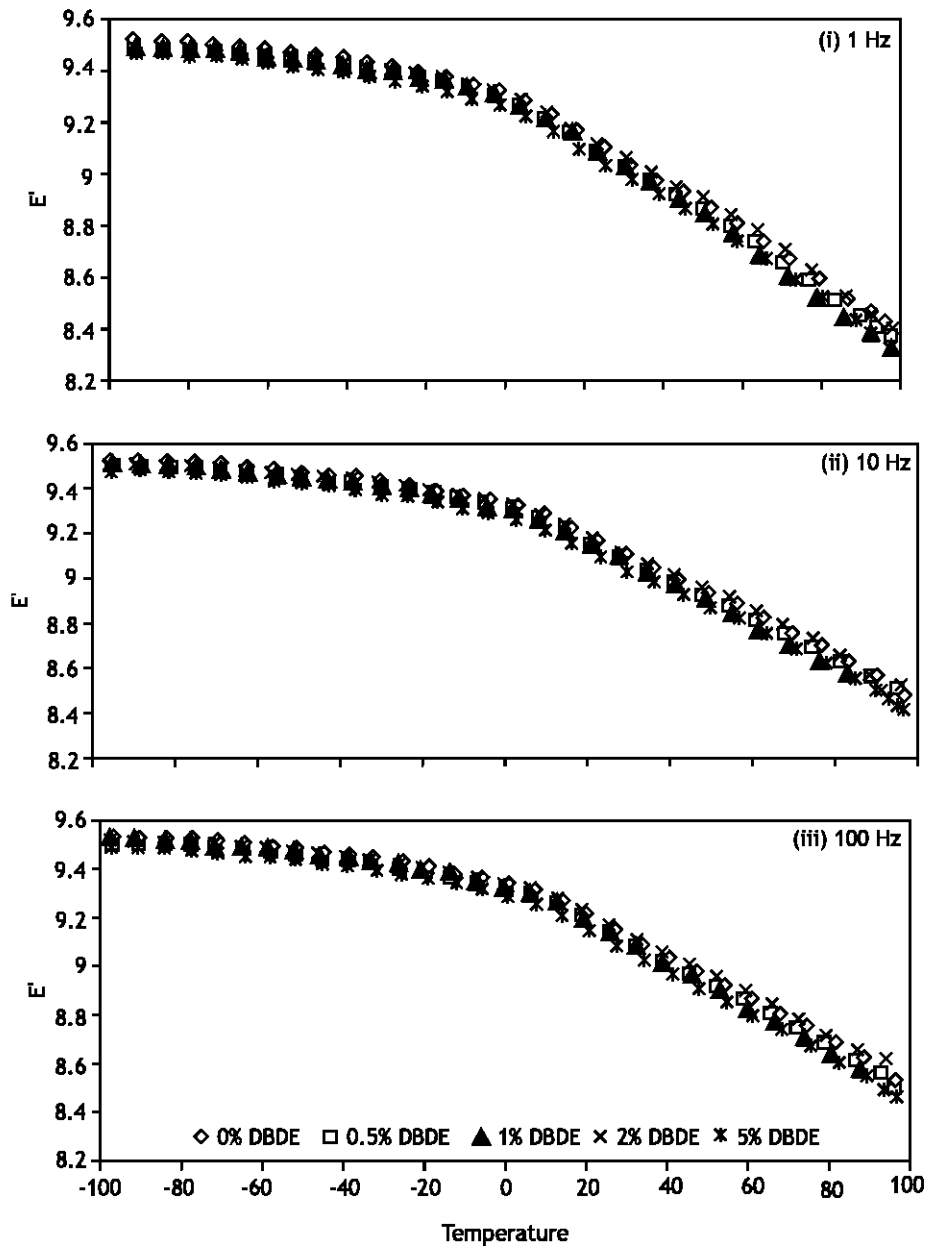


Fig. 3a: E' vs temperature for PP (5% glycerol) with various % DBDE at (i) 1 Hz (ii) 10 Hz (iii) 100 Hz

the transition temperature (below -20°C as indicated by the $\tan \delta$ versus temperature in Fig. 4b) the intermediate mixtures between 1-2% DBDE increased E' slightly higher than 0.5% DBDE blend but it is still below the 0% DBDE (with 10% glycerol) PP blend. Above the transition temperature, as the phase become rubbery the E' series decrease systematically with the content of DBDE.

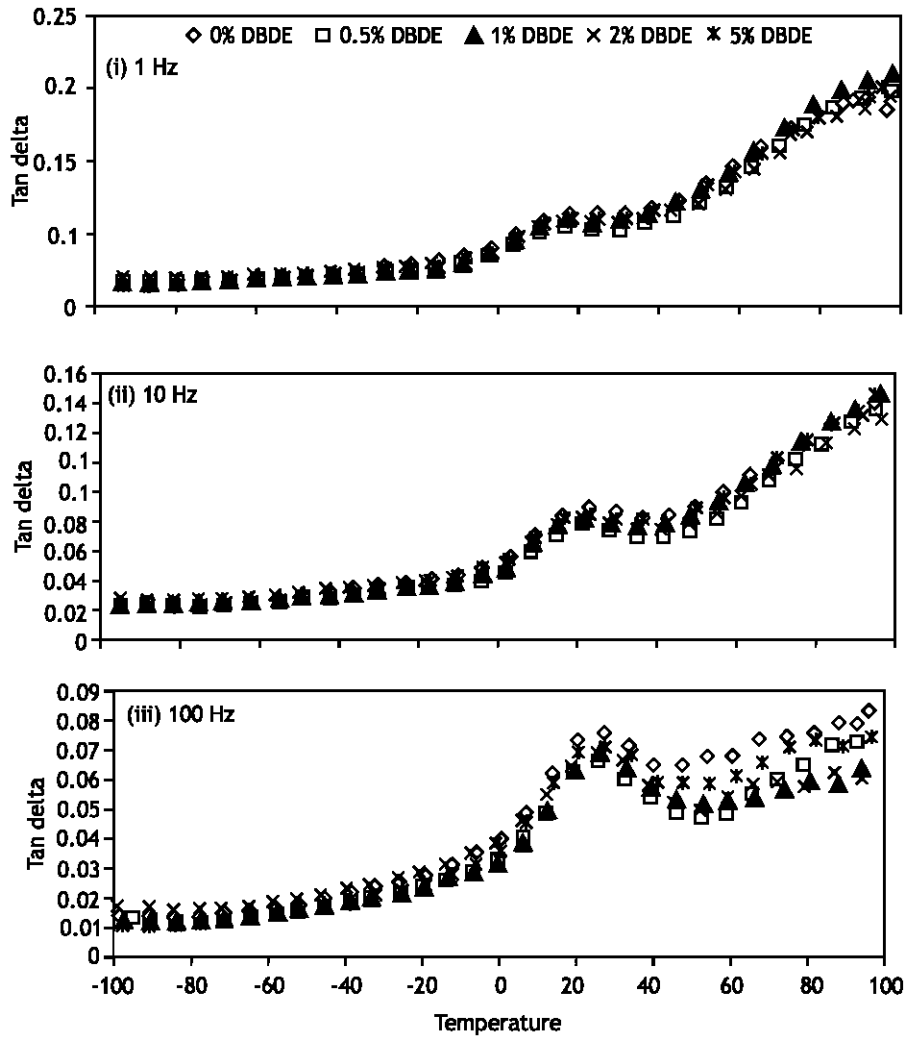


Fig. 3b: Tan delta vs temperature for PP (5% glycerol) with various % DBDE at (i) 1 Hz (ii) 10 Hz (iii) 100 Hz

Scanning electron microscopy (SEM)

Scanning Electron Microscopy (SEM) was done on each series of specimen. Fig. 5 and 6 showed the SEM micrograph of pure PP and PP samples (without glycerol) with 2% DBDE respectively. The addition of DBDE appeared as bright particles in the phase. According to Vaccaro *et al.* (1996), blending should not affect the properties of the pure component. Therefore, the surface of the sample was similar to pure PP except the presence of DBDE particles. Fig. 7 and 8 showed the SEM micrograph of PP (with 2% DBDE) containing 5 and 10% glycerol, respectively. The surfaces of these two samples were similar due to the small different

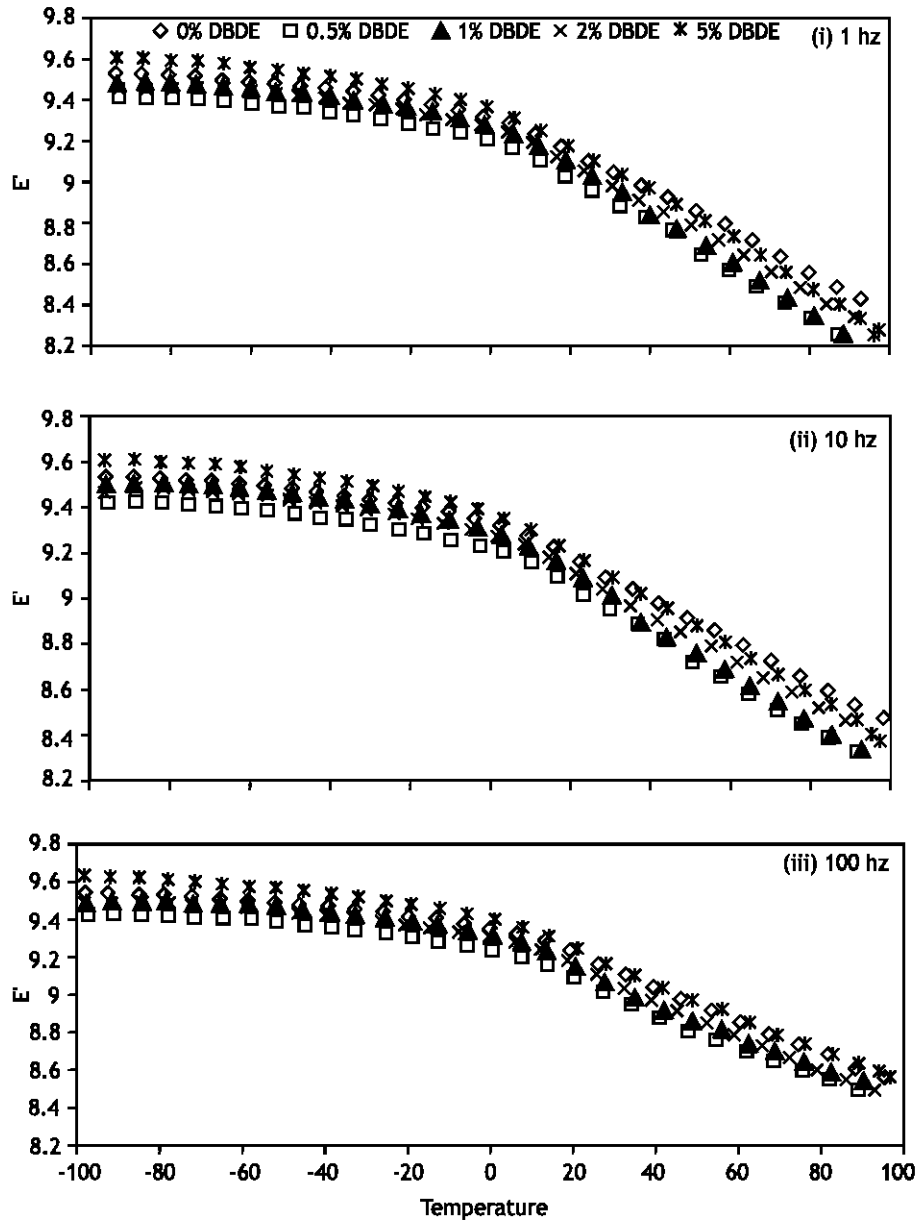


Fig. 4a: E' vs temperature for PP (10% glycerol) with various % of DBDE at (i) 1 Hz (ii) 10 Hz (iii) 100 Hz

in the % of glycerol. Nevertheless, the DBDE particles are well dispersed in the presence of glycerol. In Fig. 8, the narrow fissure on the upper right corner may be caused by the fragmentation during preparation for the SEM specimen.

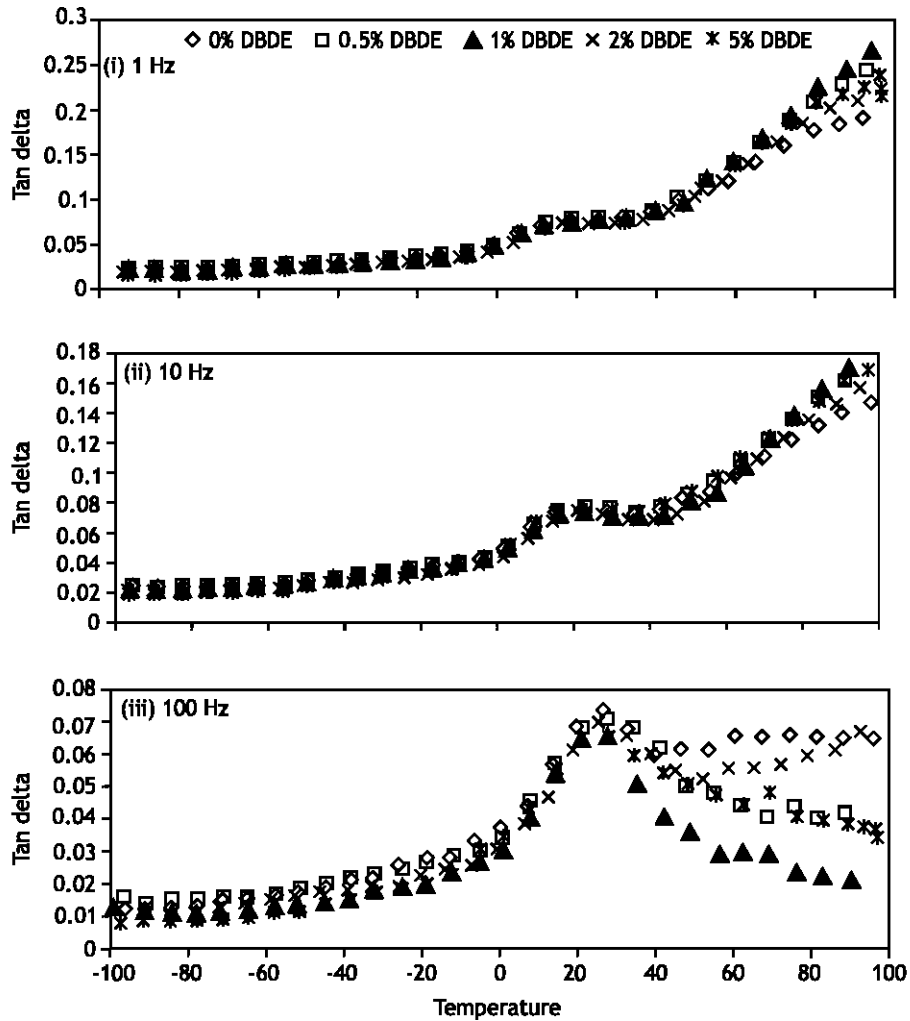


Fig. 4b: Tan delta vs temperature for PP (10% glycerol) with various % of DBDE at (i) 1 Hz (ii) 10 Hz (iii) 100 Hz

For series A specimen, pure PP (0% glycerol and 0% DBDE), yielded the highest E' and the 2% DBDE gave the lowest (most degradable) E' . 5% DBDE in series B specimen (5% glycerol) produced the lowest E' while in series C specimen (10% glycerol), 5% DBDE yielded the highest E' . For series C specimen, 0.5% DBDE yielded the lowest E' (the most degradable blend). Below the transition temperature E' did not decrease systematically with increasing percentage of DBDE for series C specimen. In fact, 0.5% DBDE yielded the minimum E' value and increased of DBDE to 1% tend to increase E' . Although E' decreased again at 2% DBDE eventually at 5% DBDE, E' appeared to

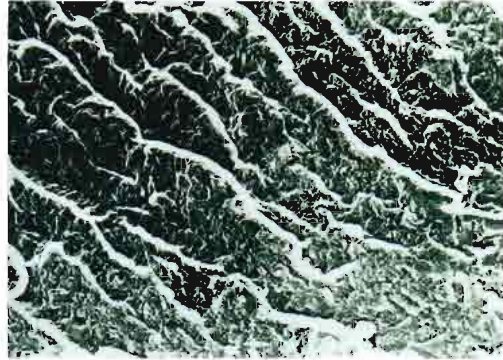


Fig. 5: SEM micrograph of pure PP

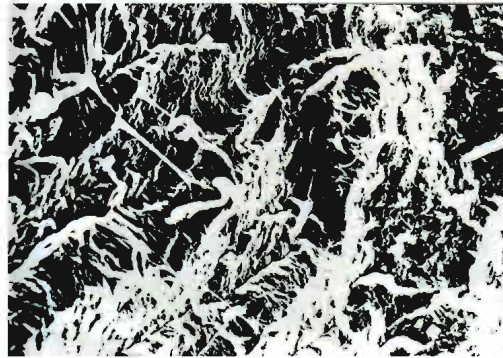


Fig. 6: SEM micrograph of PP (without glycerol) with 2% DBDE

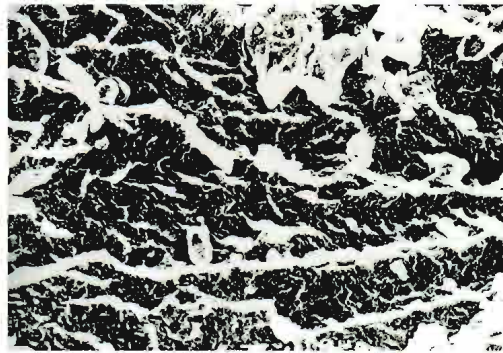


Fig. 7: SEM micrograph of PP (with 5% glycerol) with 2% DBDE

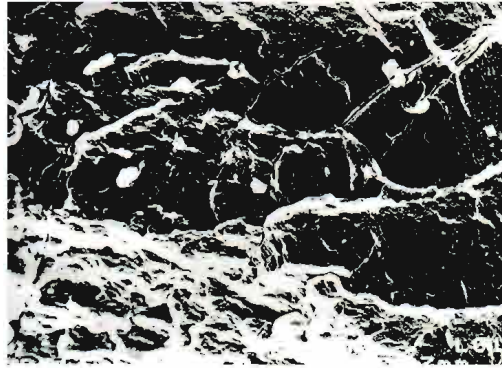


Fig. 8: SEM micrograph of PP (with 10% glycerol) with 2% DBDE

be the maximum, that was higher than 0% DBDE blend. Above the transition temperature as the phase become rubbery the C series decrease systematically with the content of DBDE. SEM micrographs reveal that DBDE has accelerated the degradation process while glycerol had disrupted the surface texture/morphology due to the plasticizing effect.

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